Chemical and isotopic composition of a speleothem from a cave in Western Germany

Martin Dietzel[1], Bettina Wiegand[2], and Wilfried Rosendahl[2]

[1]Göttinger Zentrum Geowissenschaften, Goldschmidtstr.1, 37077 Göttingen, Germany
(mdietze@gwdg.de)
[2]Göttinger Zentrum Geowissenschaften, Goldschmidtstrasse 3, 37077 Göttingen, Germany
[3]Geologisch-Paläontologisches Institut. Technische Universität Darmstadt, Schnittspahnstraße 9, 64287 Darmstadt, Germany

Speleothems are formed when $CaCO_3$ is precipitating from solutions seeping into limestone caves. They may be used in order to reconstruct the boundary conditions of natural surroundings with respect to the geological past, e.g. precipitation environment, sources of components, and paleoclimate. Information about the specific conditions and the geological age are obtained by the chemical and isotopic composition of the precipitated solid.

In the present study an 80 cm stalagmite was collected from the cave "Pfingsthöhle" in Western Germany NE Hillesheim (Rosendahl and Wiegand, 2000). The cave is located in middle Devonian limestone. Twenty samples were prepared from outer to inner sectors of the stalactite for mineralogical (X-ray diffraction) and chemical analysis (ICP-OES and ICP-MS). Isotopic ratios $^{18}O/^{16}O$, $^{13}C/^{12}C$, $^{87}Sr/^{86}Sr$, and $^{230}U/^{234}Th$ (TIMS) were measured via mass spectrometry.

The precipitation of speleothems is related to various processes. At a first stage meteoric water is saturated with biogenic carbon dioxide at a CO_2 partial pressure $P_{CO2} \approx 10^{-1.5}$ atm in the soil zone and dissolves the underlying limestone according to the overall reaction

$$CO_{2(gas)} + H_2O + CaCO_3 = Ca^{2+} + 2HCO_3^- \qquad (1)$$

In most natural environments dissolution of limestone occurs essentially under closed system conditions with respect to the CO_2-gas of the soil zone. Typical compositions of calcium bicarbonate solutions generated in catchment areas of marine carbonate results in solution saturated with respect to calcite at a pH of about 8. At this pH total dissolved inorganic carbonate (DIC) consists mostly of HCO_3^-.

As the calcium bicarbonate solution enters the cave CO_2 desorbs from the solution into the cave atmosphere which exhibits about two orders of magnitude lower P_{CO2} than the soil atmosphere above the cave. This leads to an increase of CO_3^{2-} / HCO_3^- ratio so that saturation with respect to calcite is exceeded and calcite is precipitated. Thus precipitation of $CaCO_3$ in caves may be induced by CO_2 degassing according to the overall reaction (1) from the right to the left. Moreover release of H_2O due to evaporation may promote deposition of $CaCO_3$.

In the present case the solids consist of solely calcite with 100 ±2 wt% $CaCO_3$. The magnesium and strontium contents are about 315 ±29 mg Mg and 151 ±19 mg Sr per kg solid representing the specific composition of the drip water at the time of precipitation (e.g. Huang and Fairchild, 2001). The speleothem displays growth layers with various band thickness which may be related to the growth rate controlled by the drip rate and supersaturation. The highest variation of element concentrations were measured for iron from 17 up to 1080 mg Fe per kg solid. A significant correlation exists between copper and zinc which is given by the expression: Zn =

0.534 · Cu + 0.082 (mmol metal per kg solid). Moreover a correlation exists for barium and strontium as well as for sodium and potassium.

Following the isotopic evolution of carbon, dissolved carbonate is about a (1:1) mixture of the isotopic composition of the soil-CO_2 and the limestone assuming closed system conditions with respect to CO_2-gas of the soil zone (see equation 1). Considering the $^{13}C/^{12}C$ ratio of the limestone ($\delta^{13}C_{limestone} \approx 1$ $^0/_{00}$, PDB) and of the soil-CO_2 ($\delta^{13}C_{soil-CO2} \approx -20$ $^0/_{00}$) a $\delta^{13}C_{DIC} \approx -10.5$ $^0/_{00}$ is obtained. Fractionation between precipitated calcite and DIC may be neglected if calcite is precipitating from a supersaturated solution (e.g. Dandurand et al., 1982; Dietzel et al., 1992). Following this assumption the measured mean isotopic composition of the precipitated calcite is $\delta^{13}C_{CaCO3} \approx -10.67$ $^0/_{00,}$ which reflects the isotopic value of the DIC. Similar results are obtained from isotopic studies on recent calcite precipitating springs located in areas of marine limestone (e.g. Usdowski et al., 1979). The very low $\delta^{13}C_{CaCO3}$ variation, standard deviation of about 0.36 $^0/_{00}$, represents a constant surface cover by plants and a similar kind of biogenic activity within the time period of $CaCO_3$ deposition.

The kind of $CaCO_3$ source with respect to the dissolved limestone may be followed by the $^{87}Sr/^{86}Sr$ ratio of the solids. The strontium isotopic composition was analysed for 7 samples from the inner to the outer section of the stalagmite. The $^{87}Sr/^{86}Sr$ ratio shows small variation from 0.70861 to 0.70870. These values exhibit the isotopic composition of the overlying Devonian limestone. The small range of variation represents a constant source of dissolved limestone for the growth of the speleothem.

In contrast to isotopes of carbon and strontium $^{18}O/^{16}O$-isotopic composition of the precipitated $CaCO_3$ is controlled by temperature and oxygen composition of H_2O. The drip water itself is derived from meteoric water. Thus oxygen isotope signals in speleothems are related to the local surface climate conditions, the percolating system, and the condition at the precipitation of $CaCO_3$ in the cave. The isotopic composition of the speleothem varies in the range from $\delta^{18}O_{CaCO3} = 23.89$ to 25.33 $^0/_{00}$ (SMOW) with a average value of 24.74 ±0.34 $^0/_{00}$. Considering the present average composition of meteoric water in the area of $\delta^{18}O_{H2O} = -7$ $^0/_{00}$ and assuming isotopic equilibrium (O`Neil, 1970) a temperature in the cave between 13.4 and 7.3 °C is calculated (average temperature: 9.7 °C). Additional processes may influence the oxygen isotopic composition of the precipitated calcite, e.g. variation of $^{18}O/^{16}O$ ratio of the meteoric water, precipitation and evaporation effects.

Finally the present stalagmite was analysed by $^{230}U/^{234}Th$ dating technique (TIMS) which yields very precise geological ages. Two samples were prepared, one from the top and the other from the inner section of the stalagmite basis. The growth of the speleothem began at 7530 ±270 years before present (B.P.) and stopped at 1640 ±58 years B.P.

If the above geological time period of speleothem formation is applied to the chemical and isotopic composition of the calcite it may be concluded that within ≈ 6.000 years of $CaCO_3$ deposition steady boundary conditions of the precipitation environments prevailed. Moreover the sources for solid $CaCO_3$ as biogenic CO_2 from the soil zone and dissolved limestone are very constant. Keeping in mind the uncertainty of oxygen isotopic ratios the $\delta^{18}O_{CaCO3}$ values of the precipitated $CaCO_3$ show a slight decrease of temperature from the Atlanticum to the Middle Ages, the time period of speleothem growth.

References:

Dandurand J. L., Gout R., Hoefs J., Menschel G., Schott J., and Usdowski E., 1982, Chem. Geol. 36: 299-315.
Dietzel M., Usdowski E., and Hoefs J., 1992, Applied Geochemistry 7: 177-184.
Huang Y. and Fairchild I. J., 2001, Geochim. Cosmochim. Acta 65: 47-62.
O'Neil J. R. in Friedmann I., 1970, Geochim. Cosmochim. Acta 34: 1303-1317.
Rosendahl W. and Wiegand B., 2000, Mainzer naturwiss. Archiv 38: 29-41.
Usdowski E., Hoefs J., and Menschel G., 1979, Earth Planet. Sci. Lett. 42: 267-276.